^{14}N NQR lineshape in nanocrystals: An *ab initio* investigation of urea

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^{14}N nuclear quadrupole resonance (NQR) lineshapes mostly contain information of low interest, although in nanocrystals they may display some unexpected behaviour. In this work, we present an *ab initio* computational study of the ^{14}N NQR lineshapes in urea nanocrystals as a function of the nanocrystal size and geometry, focusing on the surface induced broadening of the lineshapes. The lineshapes were obtained through a calculation of the electric field gradient for each nitrogen site in the nanocrystal separately, taking into account the individual crystal field by embedding the molecule of interest in a suitable lattice of point multipoles representing other urea molecules in the nanocrystal. The small influence of distant molecules is found with a series expansion, using the in-crystal Sternheimer shieldings which we also calculated *ab initio*. We have considered nanocrystals with two geometries: a sphere and a cube, with characteristic sizes between 5 and 100 nm. Our calculations suggest that there is a dramatic difference between the linewidths for the two geometries. For spheres, we find a steep drop in linewidths at ~ 10 nm; at 5 nm the linewidth is ~ 11 kHz, whereas for sizes above 20 nm the linewidth is practically negligible (< 100 Hz). For cubes, on the other hand, we find a steady $1/\text{size}$ decrease, from 12 kHz at 10 nm to 1.2 kHz at 100 nm. This analysis is important for ^{14}N NQR spectroscopy of crystalline pharmaceuticals, where nanoparticles are increasingly more often embedded in some sort of matrix. Although this is only a theoretical analysis, we believe that this work can serve as a guidance for the forthcoming experimental analysis. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4983484>]

I. INTRODUCTION

^{14}N Nuclear Quadrupole Resonance (NQR) spectroscopy of nitrogen containing molecular crystals is nowadays used predominantly for validation of *ab initio* and density functional theory (DFT) calculations of molecular electronic structures in crystals.^{1–7} To a lesser extent, ^{14}N NQR is used also for identification and quantification of nitrogen containing molecular crystals in heterogeneous compounds,^{8,9} e.g., discriminating between crystalline and amorphous structures, between polymorphs,^{10,11} hydrates and anhydrides,^{12,13} co-crystals,¹⁴ and others.

In bulk, the ^{14}N NQR resonances are very narrow, less than 1 kHz wide, so the parameter of interest is the ^{14}N NQR frequency, which is compound and crystal structure specific and is confined to a range between few kHz and ~ 5 MHz. Many *ab initio* studies have been published to date whose aim was to reproduce the experimentally observed ^{14}N NQR frequencies or parameters, e.g., Ref. 15. Practically all of them are concerned with calculations of the electric field gradient (EFG) at the nitrogen site in bulk, from which the ^{14}N NQR frequencies are easily obtained. A typically achieved agreement is around 10%, and is most often limited by molecular vibrations/librations not taken into account, rather than the shortcomings of the *ab initio* approach.

In nanocrystals we still expect to observe the ^{14}N NQR resonances, although some size effects, which would

prevent this observation cannot be excluded. Namely, nitrogen nuclei close to the surface experience a different environment than those in bulk. As a result, their individual NQR frequency will be shifted from the bulk frequency, which will eventually result in broadening (or perhaps shift) of the resonance. Small amounts of broadening are not much of an issue, however, as the linewidths exceed ~ 10 kHz, which is a typical ^{14}N NQR bandwidth, the resonances become very difficult to spot. The problem is an even lower S/N ratio than normal. Double resonance techniques do allow for the observation of wider ^{14}N resonances, but at the expense of accuracy and the ability to provide quantitative information.

The failure to detect some nanocrystals, e.g., smaller ones, but not the larger ones can have serious consequences for the interpretation of otherwise simple ^{14}N NQR spectra and could undermine the reputation of NQR as non-sensitive to the physical form of the sample. This problem has become relevant for ^{14}N NQR spectroscopy only recently, when pharmaceutical substances, which are often nitrogen containing molecular crystals and can be studied with ^{14}N NQR,^{8,11,16,17} became increasingly more often prepared as nanocrystals embedded in some sort of matrix. Nanocrystals are here preferred due to their large surface area, which increases the dissolution rates, and are of particular importance for poorly water soluble molecules. The latter are estimated to comprise $\sim 40\%$ of all APIs. So far, there have been no reports on any observation of classical ^{14}N NQR in nanocrystals, so that the extent of size-dependent broadening is not known. There is however a ^{14}N NQR study of a single 30-nm thick flake of

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hexagonal boron nitride,¹⁸ where the detection was accomplished through a nitrogen vacancy center in diamond used as a sensitive, atomic-scale magnetic field sensor. Here, the ^{14}N NQR signal of a nanocrystal is observable however, the quadrupole couplings involved are very small (~ 150 kHz) and make the corresponding size-dependent broadening small compared to other broadening mechanisms and thus difficult to observe.

In order to provide some insight into the subject, we decided to theoretically investigate the size-lineshape relationship of the ^{14}N NQR resonance in nanocrystals with *ab initio* techniques. The aim was to provide quantitative parameters relating the surface induced broadening and nanocrystal size. We have chosen urea for this study. Urea is a small molecule with a simple crystal structure and should therefore facilitate *ab initio* calculations. In addition, urea has a strong ^{14}N NQR signal and is because of this a good candidate to use in future experimental studies. Since ^{14}N NQR is not a sensitive technique, one cannot hope to detect individual nanocrystals, but rather macroscopic ensembles of nanocrystals. If these nanocrystals are sufficiently separated among themselves, then one can consider each individual nanocrystal to be an isolated nanocrystal. Further on, if the nanocrystals are also reasonably uniform in size and shape, then the ensemble NQR lineshape should represent also the otherwise unobtainable lineshape of an isolated nanocrystal of a given size and shape.

We choose two nanocrystal geometries, a sphere and a cube, and calculated the EFG tensor for each nitrogen site within an isolated nanocrystal for several nanocrystal sizes. The EFG's are calculated *ab initio* with the second-order Møller-Plesset (MP2) perturbation approximation. The crystal field effects were modeled by embedding a single urea molecule in a lattice of point multipoles representing the charge distributions of other urea molecules in the nanocrystal. In principle, one would have to do an *ab initio* calculation for each molecule in the nanocrystal separately, using its own arrangement of neighboring molecules, which takes into account the finite size of the nanocrystal. This would however

consume a lot of resources. Instead, we reduced the number of *ab initio* calculations by calculating the EFG for similar environments with a series expansion for which we calculate the coefficients *ab initio*. The found EFGs are then used to predict the width of the ^{14}N NQR resonance as the nanocrystals increase in size.

II. MODELS AND METHODS

The urea crystal is tetragonal with the space group $P\bar{4}_21m$ and lattice parameters $a = b = 5.645$ Å and $c = 4.704$ Å at room temperature. There are two urea molecules in the unit cell ($Z = 2$), and each urea molecule contains two nitrogens, all nitrogens are crystallographically equivalent. The molecular structure and the here used molecular coordinate system are shown in Fig. 1(a) while the unit cell in Fig. 1(b). In all calculations we use the published structure by Guth *et al.*¹⁹ at 293 K.

We consider two nanocrystal geometries with sizes up to 200 unit cells: (i) a spherical nanocrystal, consisting of approximately equal number of unit cells in each direction and (ii) a cubic nanocrystal, consisting of the same number of unit cells in each of the three crystallographic axes.

The EFG for a nitrogen site of interest in the nanocrystal is calculated with the embedded molecule approach, where the molecule containing the nitrogen site (the *ab initio* molecule) is embedded in a lattice of multipoles representing the charge distribution of other urea molecules in the nanocrystal (the lattice molecules). Lattice molecules close to the *ab initio* molecule are represented with multipoles positioned at each atomic site of the molecule, hereafter referred to as point multipoles. The remaining lattice molecules are represented by an equivalent electric field, EFG, and electric field hyper gradient. These fields are calculated using point multipoles or a simpler multipole representation for the molecule with multipoles located only on the carbon site, hereafter referred to as molecular multipoles. The charge distribution of all urea molecules in the nanocrystal (the *ab initio* molecule excluded) is assumed to be equal and

FIG. 1. In (a), the urea molecule and the molecular coordinate system, (b) the urea unit cell, and (c) a view along the crystallographic c axis of the urea crystal, showing the first few cubic layers around the molecule in the center. A solid line links the centers of all molecules that belong to the same layer. There are 8 molecules in layer 1, 26 molecules in layer 2, and 56 molecules in layer 3. Here, only molecules in two planes running perpendicular to the c axis are shown.

corresponding to the charge distribution of a molecule in bulk.

The molecules around the *ab initio* molecule are grouped into cubic layers as shown in Fig. 1(c) (molecules within a single layer are all parallel). The occupancy of each layer depends on the *ab initio* molecule position within the nanocrystal.

The EFG for a nitrogen site in the *ab initio* molecule embedded in at least n layers, where the first n layers are fully occupied, is calculated with a series expansion^{20,21}

$$V_{\alpha\beta} = V_{\alpha\beta}^{(n)} + g_{\alpha\beta,\gamma}F_{\gamma} + \left(\frac{1}{2}(\delta_{\alpha\delta}\delta_{\beta\gamma} + \delta_{\alpha\gamma}\delta_{\beta\delta}) + g_{\alpha\beta,\gamma\delta}\right)F_{\gamma\delta} + g_{\alpha\beta,\gamma\delta\epsilon}F_{\gamma\delta\epsilon} + \frac{1}{2}\epsilon_{\alpha\beta,\gamma,\delta}F_{\gamma}F_{\delta} + \frac{1}{6}\phi_{\alpha\beta,\gamma,\delta,\epsilon}F_{\gamma}F_{\delta}F_{\epsilon} + \dots \quad (1)$$

Here, $V_{\alpha\beta}^{(n)}$ is the EFG contribution due to molecules in the first n layers, whereas molecules in the remaining layers are taken into account indirectly through the electric field F_{α} and its derivatives $F_{\alpha\beta}$, $F_{\alpha\beta\gamma}$ produced at the nitrogen site of interest. The expansion coefficients $g_{\alpha\beta,\gamma}$, $g_{\alpha\beta,\gamma\delta}$, and $g_{\alpha\beta,\gamma\delta\epsilon}$ are known as the generalized Sternheimer (anti)shields, while $\epsilon_{\alpha\beta,\gamma,\delta}$ and $\phi_{\alpha\beta,\gamma,\delta,\epsilon}$ as the EFG polarizabilities and hyperpolarizabilities, respectively. All expansion coefficients are, similarly as $V_{\alpha\beta}^{(n)}$, a function of n , although this is not explicitly shown. In a similar way, $V_{\alpha\beta}$, F_{γ} , $F_{\gamma\delta}$, ... depend on the nitrogen site location in the nanocrystal, but this is not explicitly shown. In Eq. (1), the indexes α , β , ... refer to the Cartesian directions x , y , and z , while we use the Einstein convention of sums over repeated indices. The expansion coefficients ($V_{\alpha\beta}^{(n)}$ and the shields) are calculated *ab initio*, where we use the finite field (FF) method to determine shields. We will hereafter refer to the approximation in Eq. (1) as the Sternheimer approximation, even though it contains some nonlinear terms, which are not described with the generalized Sternheimer (anti) shields.

The number of shields required to describe a molecule is in general large. For example, there are 15 $g_{\alpha\beta,\gamma}$, 25 $g_{\alpha\beta,\gamma\delta}$, and 35 $g_{\alpha\beta,\gamma\delta\epsilon}$ coefficients.²⁰ For symmetric sites, the number of independent coefficients is smaller, for the nitrogen site in urea (C_s symmetry) we have: 8 $g_{\alpha\beta,\gamma}$, 13 $g_{\alpha\beta,\gamma\delta}$, and 18 $g_{\alpha\beta,\gamma\delta\epsilon}$. The two nitrogen sites in the urea molecule, which are crystallographically equivalent, are equivalent also when embedded in fully occupied cubic layers as defined in Fig. (1). Thus both $V_{\alpha\beta}^{(n)}$ and the shielding parameters for the two sites are related: quantities with an even number of z indexes are equal for both nitrogen sites, whereas, quantities with an odd number of z indexes have opposite signs.

We inspect five values for n , $n = 0 \dots 4$. However, as we will show, a single value ($n = 2$) is sufficient to describe the nanocrystal NQR linewidth adequately.

The urea charge distribution in bulk is found self-consistently for a molecule embedded in 100 fully occupied layers. This charge distribution is found with an iterative approach, starting with a charge distribution for an isolated molecule and finding a new distribution in each iteration until this converges. We here use the Stone's distributed multipole analysis²² to find the point multipoles, which are then used to calculate the molecular multipoles.

We focus only on the highest ^{14}N (spin $I = 1$) NQR transition, with a frequency

$$\nu_+ = \frac{3}{4}C_q\left(1 + \frac{1}{3}\eta\right), \quad (2)$$

which is referred to as the NQR frequency. The results for ν_- should be similar, whereas ν_0 is typically very low and thus not interesting. The ν_+ frequency is related to the EFG through the quadrupole coupling constant $C_q = e^2qQ/h$ and the EFG tensor asymmetry parameter η , where eq is the EFG largest principal component, while Q is the electric quadrupole moment of the ^{14}N nucleus. We will here use $Q = 0.02$ b but keep in mind that this value is not known very accurately.

All *ab initio* calculations were done with the Firefly QC package,²³ which is partially based on the GAMESS (US)²⁴ source code. We used the aug-cc-pVDZ and aug-cc-pVTZ basis sets and correlate only valence electrons in the MP2 calculations. The Firefly input files were prepared with Mathematica, as these are especially cumbersome when embedded multipoles are being used.

III. RESULTS AND DISCUSSION

A. Bulk properties

We first calculated the charge distribution (point and molecular multipoles) for an urea molecule in bulk at the Hartree-Fock (HF) and MP2 levels of theory using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. The molecular multipoles are shown in Table I, whereas the point multipoles in the [supplementary material](#). The bulk EFG tensors and the associated NQR parameters, which are also found during these calculations, are shown in Table II.

The inspection of the results reveals that the molecular dipole moment (p_z) is not very sensitive to the level of theory and the basis set, the variations are less than 2%. The values we find are in perfect agreement with calculations by Santos *et al.*²⁵ which also used embedded molecules, their MP2/aug-cc-pVDZ $p_z = -2.966$ a.u. is very close to $p_z = -3.013$ a.u. calculated here. The in-crystal dipole moment is a rather difficult quantity to determine experimentally. Birkendal *et al.*²⁶ used synchrotron diffraction and fitted the data to a multipole expansion model for the urea molecule. Their

TABLE I. The calculated and experimental molecular dipole moment (p_z) and quadrupole moment components q_{xx} and q_{yy} ($q_{zz} = -q_{xx} - q_{yy}$) for the urea molecule in bulk. The nonlisted components are 0 due to the C_{2v} symmetry. The origin for the quadrupole moment is at the carbon site.

	p_z (a.u.)	q_{xx} (a.u.)	q_{yy} (a.u.)
HF/aug-cc-pVDZ	-3.058	16.823	-10.620
HF/aug-cc-pVTZ	-3.054	16.894	-10.454
MP2/aug-cc-pVDZ	-3.013	16.719	-10.833
MP2/aug-cc-pVTZ	-3.009	16.909	-10.756
MP2/aug-cc-pVDZ	-2.966 ^a		
Experimental	-2.457 ^b		

^aA value of 7.54 D is found by Santos *et al.*²⁵ in their *ab initio* study. They use a different procedure to calculate the molecule charge distribution.

^bDetermined from the molecular analysis of synchrotron diffraction data²⁶ at 123 K; $d_z = -1.30(11)$ eÅ.

TABLE II. The calculated EFG tensors (in a.u.) and the associated NQR parameters for the urea molecule in bulk and for the isolated molecule, together with the NQR experimental values at room temperature.

	Bulk				Experiment	Isolated molecule ^a MP2/aug-cc-pVTZ
	HF		MP2			
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ		
V_{yy}	0.9169	0.8774	0.7819	0.7788	...	0.9839
$V_{xx} - V_{zz}$	−0.0821	−0.0855	−0.0755	−0.0850	...	0.0185
V_{xz}	0.0897	0.0942	0.0815	0.0938	...	0.0311
C_q (kHz)	4308.63	4123.13	3674.23	3659.56	3412.3	4411.94
η	0.22	0.24	0.23	0.26	0.3131	0.07
ν_+ (kHz)	3463.2	3335.4	2966.7	2986.5	2826	3385.2
ν_- (kHz)	2999.7	2849.3	2544.7	2502.8	2292	3232.7
ν_0 (kHz)	463.5	486.1	422.0	483.8	534	152.6

^aUsing crystal geometry.

$p_z = -2.457$ a.u. is reasonably close to the values calculated in this study. Contrary to p_z , we do observe substantial variations of the point multipoles (supplementary material) determined in different cases. This is however expected and is due to the Stones's distributed multipole analysis used here, which is known to be very basis set dependent. Nevertheless, these variations are not reflected in the electrostatic potential outside the molecule, which is relevant for our calculations. The potential was shown to converge upon increasing the basis sets.²⁷

The EFG tensors shown in Table II correspond to the ^{14}N atom on the right hand side in Fig. 1(a), whereas the NQR parameters are the same for both ^{14}N nuclei in the molecule. The variations between the EFG components are larger for HF calculations than they are for the MP2 calculations upon a change of the basis set. Unfortunately we cannot make a comparison with experimental values because these have not been determined for urea (as it is generally the case for ^{14}N). We thus restrict our comparison to NQR parameters C_q and η .

The HF C_q values for both basis sets are significantly larger than the experimental C_q , the aug-cc-pVDZ by 26% and the aug-cc-pVTZ by 20%, with an apparent trend toward the experimental value for larger basis sets. The MP2 values are much closer to the experimentally determined value, for both basis sets they are $\sim 7\%$ larger. The difference between the values for the two basis sets is small and amounts to $\sim 0.4\%$ with a trend toward the experimental value. We were not able to use an even larger basis set to see if the trend persists; however, based on the extrapolation of the above results, it is unreasonable to expect that only an increase of the basis set would bridge the gap. The differences between the HF and MP2 calculations found here are in agreement with the studies by Coriani *et al.*,²⁸ who found that the electron correlation is non-negligible for the EFG calculations, although the effects are not dramatic. In a separate calculation (not shown), we also included octupoles in the multipole description of the urea molecule, but the changes in the parameters were smaller than 0.5%. The discrepancy between the MP2 values and experimental results is in our opinion rather small, given the approximations that were used in the *ab initio* calculations (the embedded molecule) and the complete neglecting of lattice vibrations and molecular

librations. The later process alone can change C_q by as much as 5%.

The asymmetry parameter η is found to be much smaller than the experimentally observed η in all cases. Similarly as for C_q , the discrepancies are most likely due to crystal field approximations and unaccounted lattice vibrations and/or molecular librations.

In Table II we show also our MP2/aug-cc-pVTZ calculation for an isolated urea molecule, with the same geometry as in bulk (the urea geometry in gas is slightly different). These results can be used to determine the influence of crystal fields. We find that crystal fields have a non-negligible influence on the EFG, as all components change substantially. The difference between the two C_q is quite large, we observe a reduction upon embedding the molecule by 17%, which is within the range of values typically observed for small molecules.²⁹ The influence of the crystal field on η is rather dramatic, it changes from $\eta = 0.07$ in an isolated molecule to $\eta = 0.26$ in bulk.

B. The Sternheimer approximation in a crystalline environment

The expansion coefficients $V_{\alpha\beta}^{(n)}$, $g_{\alpha\beta,\gamma}$, $g_{\alpha\beta,\gamma\delta}$, $g_{\alpha\beta,\gamma\delta\epsilon}$, and $\epsilon_{\alpha\beta,\gamma,\delta}$ were calculated at the MP2 level of theory using the aug-cc-pVTZ basis set for $n = 0, 1, 2, 3$, and 4. In Table III we list: $V_{\alpha\beta}^{(n)}$, $g_{\alpha\beta,\gamma}$, and $g_{\alpha\beta,\gamma\delta}$ for $n = 0, 2, 4$. The linear parameters $g_{\alpha\beta,\gamma\delta}$ were calculated using 5 independent EFGs with nonzero components $F_{\gamma\delta} = \pm 0.0006$, whereas for $g_{\alpha\beta,\gamma\delta\epsilon}$ we used 7 independent electric field hyper gradients with nonzero components $F_{\gamma\delta\epsilon} = \pm 0.0002$. For $g_{\alpha\beta,\gamma}$ and $\epsilon_{\alpha\beta,\gamma,\delta}$, which were calculated together, we used 112 electric fields with $0 \leq F_x \leq 0.003$, $0 \leq F_y \leq 0.003$, and $|F_z| \leq 0.003$ in increments of 0.001. We here took advantage of the molecular symmetry by utilizing the EFGs of both ^{14}N in the urea molecule.

Inspecting Table III one notes that there is a significant difference between the $V_{\alpha\beta}^{(n)}$ values for an isolated molecule and the embedded ones, whereas there is a very small difference between the embedded molecules and the bulk $V_{\alpha\beta}$ found previously. For the Sternheimer shieldings, we find an analogous situation, as expected. In a separate calculation (not

TABLE III. EFG components $V_{\alpha\beta}^{(n)}$ (in a.u.) and shieldings $g_{\alpha\beta,\gamma}$ (in a.u.) and $g_{\alpha\beta,\gamma\delta}$ for an isolated molecule ($n = 0$) and embedded molecule with $n = 2$ and $n = 4$. The nonlisted coefficients are zero due to symmetry.

	Isolated molecule	Embedded molecule	
	$n = 0$	$n = 2$	$n = 4$
$V_{yy}^{(n)}$	0.9389	0.7840	0.7828
$V_{xx}^{(n)} - V_{zz}^{(n)}$	0.0184	-0.0849	-0.0879
$V_{xz}^{(n)}$	0.0311	0.0881	0.0881
$g_{xx,x}$	2.439	3.082	3.085
$g_{xx,z}$	2.407	1.787	1.780
$g_{xy,y}$	1.196	0.883	0.887
$g_{xz,x}$	2.794	2.814	2.819
$g_{xz,z}$	0.198	-0.025	-0.027
$g_{yz,y}$	-0.932	-0.583	-0.577
$g_{zz,x}$	1.284	2.185	2.184
$g_{zz,z}$	-4.756	-4.576	-4.569
$g_{xx,xx}$	4.064	2.744	2.739
$g_{xx,xz}$	1.741	1.758	1.757
$g_{xx,zz}$	-2.027	-1.536	-1.532
$g_{xy,xy}$	1.578	1.178	1.182
$g_{xy,yz}$	0.678	0.728	0.729
$g_{xz,xx}$	0.161	0.223	0.226
$g_{xz,xz}$	2.262	2.371	2.376
$g_{xz,zz}$	-0.779	-0.869	-0.875
$g_{yz,xy}$	0.603	0.712	0.713
$g_{yz,yz}$	2.446	1.834	1.830
$g_{zz,xx}$	-3.160	-3.691	-3.692
$g_{zz,xz}$	0.191	0.222	0.223
$g_{zz,zz}$	4.358	4.148	4.147

shown), we have calculated also the Sternheimer shieldings for bulk and found that they are negligibly different from the $n = 4$ case.

In literature, there are just a few reports on Sternheimer shieldings and EFG polarizabilities for ^{14}N . The ones we found are for several linear molecules; N_2 , HCN , and HNC , and for NH_3 , all for isolated cases. The comparison of the coefficients between different molecules is usually done using two rotationally invariant coefficients $\bar{g} = \frac{1}{5}g_{\alpha\beta,\alpha\beta}$ and $\bar{\epsilon} = \frac{2}{15}\epsilon_{\alpha\beta,\alpha\beta}$, while we here introduce an additional rotationally invariant shielding $g_{RMS}^2 = \frac{2}{9}g_{\alpha\beta,\gamma}g_{\alpha\beta,\gamma}$ that can be used instead of $g_{zz,z}$ for linear molecules. A comparison between the published data and the results found here is shown in Table IV. The values for urea are within the range of values found for other molecules.

Having found the expansion coefficients, we proceed now to assess the usefulness of the Sternheimer approximation (Eq. (1)) for the calculation of EFGs in (nano)crystals. The quality of the approximation will be assessed from the NQR point of view, monitoring the ν_+ frequency for a molecule embedded in $n + 1$ layers, where the first n layers are fully occupied, while there is a single molecule in layer $n + 1$. The ν_+ frequency of such an embedded molecule is calculated twice: (i) with the embedded molecule approach using molecules in all $n + 1$ layers and (ii) using the Sternheimer approximation for a molecule embedded in n layers and perturbed by a molecule in layer $n + 1$. For each n , we find an

TABLE IV. Comparison of rotationally invariant shieldings for some small molecules and the current calculations for an isolated ($n = 0$) and embedded ($n = 2$) urea molecule.

	$\bar{g}$	$\bar{\epsilon}$ (a.u.)	g_{RMS} (a.u.)
N_2^a	-1.632	-12.23	3.580 ^b
HCN^a	2.886	-35.93	4.351 ^b
HNC^a	3.429	-14.45	4.327 ^b
NH_3^c	8.824	-56.61	3.12 ^b
Isolated urea ^d	4.846	-25.16	4.10
Embedded urea ^d	3.864	-18.71	4.52

^aCalculated by Coriani *et al.*²⁸ for SCF/d-aug-cc-pVTZ.

^bThe unpublished $g_{xz,x}$ parameters were calculated here.

^cCalculated by Bishop *et al.*³⁰ at the MP2 level.

^dMP2/aug-cc-pVTZ.

average error (the standard deviation $\sigma_+^{(n)}$) as the molecule in layer $n + 1$ is moved through all the possible positions in that layer. In addition, for each n we define $\Delta\nu_+^{(n)}$ as the difference between the largest and smallest calculated ν_+ frequency. We use $\Delta\nu_+^{(n)}$ as a rough measure for the width of the ν_+ lineshape of an embedded molecule having fully occupied layers $1 \dots n$ while having only partially occupied any remaining layers. This linewidth is primarily influenced by the occupancy of the $n + 1$ layer so that $\Delta\nu_+^{(n)}$ should give us a reasonable estimate. For an easier comparison of the linewidths, we define also $\nu_+^{(n)}$, as the ν_+ frequency of a molecule embedded in fully occupied layers $1 \dots n$, which can be calculated from the previously found $V_{\alpha\beta}^{(n)}$. For large n , $\nu_+^{(n)}$ approaches the bulk ν_+ frequency, designated by $\nu_+^{(\infty)}$. A summary of the analysis is shown in Table V.

We first inspect $\nu_+^{(n)}$ and note that $\nu_+^{(n)}$ quickly converges toward $\nu_+^{(\infty)}$ as the number of layers increases; the shift from the bulk frequency for $n = 1$ is ~ 145 kHz, for $n = 2$ it is already ~ 3 kHz, whereas for $n = 4$ it is merely ~ 150 Hz, suggesting the convergence of the NQR frequency. This very quick convergence is at least in part due to the symmetric choice of cubic layers. In fact, inspecting $\Delta\nu_+^{(n)}$, we note that although $\nu_+^{(4)} - \nu_+^{(\infty)} = 150$ Hz, the corresponding $\Delta\nu_+^{(4)} = 7.8$ kHz, that is, 50 times larger. This means that the ^{14}N NQR frequency of a molecule embedded in 4 layers is still very influenced by the configuration in layer 5. The situation is expectedly worse for smaller n as $\Delta\nu_+^{(n)}$ are much larger. Based on the values of $\Delta\nu_+^{(n)}$ from Table V, we conclude that molecules having partially filled layers 1 or 2, i.e., with $n = 0$ and $n = 1$, respectively, are most likely unobservable with NQR, regardless of the configuration in other layers, as both $\Delta\nu_+^{(0)} = 174$ kHz and $\Delta\nu_+^{(1)} = 179.5$ kHz are substantially larger than the typical NQR observation window, which is approximately 10 kHz.

By inspecting $\sigma_+^{(n)}$ in Table V, we note that the Sternheimer approximation gives surprisingly good results, with errors smaller than 30 kHz, which comprises less than 1% of the bulk frequency. The accuracy in general increases as more terms are included in the series expansion. The relative contributions from different terms can be at least conceptually determined with the use of electric fields due to a dipole at a distance r : $F_\gamma \propto p_z/r^3$, $F_{\gamma\delta} \propto p_z/r^4$, and $F_{\gamma\delta\epsilon} \propto p_z/r^5$. Upon ordering the terms in powers of r , we obtain a sequence as

TABLE V. The accuracy of the Sternheimer approximation for the calculation of ν_+ frequency in crystals as a function of n and series expansion length. The approximated EFG for each site is calculated using Eq. (1) first by using only the $g_{\alpha\beta,\gamma}F_\gamma$ terms and then progressively adding the other listed terms. The direct EFG contribution, which is not related to any shieldings, was always taken into account.

n	$\nu_+^{(n)}$ (kHz)	$\Delta\nu_+^{(n)}$ (kHz)	Approximation error $\sigma_+^{(n)}$ (kHz)					
			Point multipoles				Molecular multipoles	
			$g_{\alpha\beta,\gamma}F_\gamma$	$+g_{\alpha\beta,\gamma\delta}F_{\gamma\delta}$	$+g_{\alpha\beta,\gamma\delta\epsilon}F_{\gamma\delta\epsilon}$	$+g_{\alpha\beta,\gamma,\delta\epsilon}F_\gamma F_\delta F_\epsilon$	$g_{\alpha\beta,\gamma}F_\gamma$	$+g_{\alpha\beta,\gamma\delta}F_{\gamma\delta}$
0	3385.25	174.0	18.98	19.38	12.94	16.20	28.09	18.88
1	3131.53	179.5	26.36	6.770	3.871	4.523	25.67	11.15
2	2989.50	35.46	1.249	0.316	0.209	0.216	1.482	0.530
3	2990.20	14.60	0.548	0.113	0.021	0.018	0.576	0.190
4	2986.41	7.777	0.157	0.024	0.008	0.007	0.164	0.046
...								
∞	2986.55							

shown in Table V. However, in practice this order is not being followed at smaller n . We should also mention that the next important term in the series expansion is not $\phi_{\alpha\beta,\gamma,\delta,\epsilon}F_\gamma F_\delta F_\epsilon$ as listed in Eq. (1), but rather a cross term $\propto F_\gamma F_\delta F_\epsilon$, which is not shown in Eq. (1) and was also not included in this study. This aspect of the approximation was however not investigated further.

The best results of the Sternheimer approximation are obtained for $n = 4$ using all the calculated coefficients, where the fields are calculated using point multipoles. The error obtained is ~ 7 Hz, which we find quite impressive. The approximation is expectedly the worst for $n = 0$, as for this n , the fields are the largest and a very long series would be needed for much better results. Of interest is also the $n = 2$ case, where $\sigma_+^{(n)} < 1$ kHz, a typical value of the NQR linewidth in bulk.

For large n , it is reasonable to calculate the fields (of the molecule in layer $n + 1$) with molecular multipoles instead of point multipoles and accepting an associated increase in the error, which however decreases with n . The results of such a calculation are also shown in Table V, where we show only the approximations using the Sternheimer shieldings: $g_{\alpha\beta,\gamma}$ and $g_{\alpha\beta,\gamma\delta}$. The errors indeed increase, in general by a factor of two. But nevertheless, for $n \geq 2$ these remain below 1 kHz.

C. ^{14}N NQR lineshapes

The ^{14}N NQR lineshapes of nanocrystals and their widths were determined from ν_+ frequencies of all nitrogen sites in the nanocrystal which have fully occupied layers 1 and 2, while having an arbitrary occupation of other layers. All nitrogen sites having partially filled layer 1 or layer 2 were discarded based on our previous conclusion that their NQR frequencies are two broadly distributed to be observable with NQR. The EFG for the included nitrogen sites were calculated with the Sternheimer approximation (Eq. (1)) considering only the linear terms $g_{\alpha\beta,\gamma}$ and $g_{\alpha\beta,\gamma\delta}$ while using the $n = 2$ expansion coefficients ($V_{\alpha\beta}^{(2)}$, $g_{\alpha\beta,\gamma}$, and $g_{\alpha\beta,\gamma\delta}$) shown in Table III. The electric fields in the Sternheimer approximation were calculated using molecular multipoles shown in Table I.

The sizes (l) for the two nanocrystals geometries, cubes, and spheres, were between 10 and 200 unit cells, where for cubes l is the edge length, while for spheres l is the diameter. The largest $l = 200$ roughly corresponds to a nanocrystal of size 100 nm. In Fig. 2 we show the NQR lineshape for each geometry for $l = 100$ and the linewidth ($\Delta\nu_{1/2}$) dependence on l . The lineshapes for other l are similar to the two $l = 100$ lineshapes for each geometry separately; they are all centered at the bulk NQR frequency and essentially a wider or narrower version of the two $l = 100$ lineshapes. The presented lineshapes have been smoothed with a Gaussian function ($\Delta\nu_{1/2} = 22$ Hz).

For cubes, all lineshapes show some structure, especially the two singularities close to the center, which are probably due to ^{14}N just below the surfaces. At larger l , the two singularities come closer together; however, they are still resolved at $l = 200$. For $l = 10$, the lineshape is very broad and is most likely too wide to be observed with pure NQR. The lineshapes for $l \geq 20$ are narrower, $\Delta\nu_{1/2} < 12$ kHz so that they should be observable with pure NQR. The linewidths for cubes seem to be inversely proportional to the nanocrystal size. In Fig. 2 we show a fit obtained with

FIG. 2. Two representative ^{14}N NQR spectra and the corresponding size-line-width dependence for two nanocrystal geometries: (i) spheres (open blue circles) and (ii) cubes (open red squares). The representative spectra are calculated for a nanocrystal size of 100 unit cells.

$$\Delta\nu_{1/2} = \Delta\nu_0 \frac{l_0}{l}, \quad (3)$$

where $\Delta\nu_0 = 13.2$ kHz and $l_0 = 18.1$.

For spheres, the lineshapes are strikingly different than those for cubes. They are bell shaped curves, centered at the bulk frequency, and without any additional feature. For $l = 10$, we already find a rather narrow lineshape with $\Delta\nu_{1/2} = 11.5$ kHz, which is a value observable with pure NQR. For larger l , the linewidth steeply drops, for $l = 100$ $\Delta\nu_{1/2} = 27$ Hz, which is barely larger than the linewidth of the smoothing function.

The difference between the linewidths for the two geometries is not completely unexpected and can be rather easily explained. We model our nanocrystal with a superposition of two slightly shifted uniformly polarized objects (in this case, a cube or a sphere) with opposite polarizations. Here the two objects represent the two urea sublattices in the nanocrystal: one sublattice contains all urea molecules oriented along the $+z$ direction, whereas the other sublattice represents the remaining urea molecules, where all point in the $-z$ direction (see Fig. 1(b)). The shift of the two objects is due to the shift of the two sublattices, which coincides with the shift of the two urea molecules in the unit cell. We aim now to calculate the electric field inside the superimposed objects.

The electric field inside a uniformly polarized sphere is known to be homogeneous and pointing in the direction of the polarization. Thus, the superposition of two spheres with opposite polarization yields a zero net electric field over most of the superimposed sphere (the field is nonzero only for a very small surface region). Together with the electric field also the EFG tensor and higher derivatives are zero. Thus, all ^{14}N in our urea spherical nanocrystal experience the same (zero) electric field and as a consequence, the NQR lineshape is expected to be very narrow. In contrast, the electric field of a uniformly polarized cube is inhomogeneous and can be calculated analytically only for special cases. The inhomogeneity combined with the shift of the two cubes with opposite polarization results in a nonzero electric field throughout the superimposed cube. The electric field is still very small at the center of the cube but increases almost linearly toward its surface. We have here derived an analytical expression for the superimposed cube electric field along the z axis which passes through the center of the cube. The field at the surface of a cube with edge l_{cube} aligned with the coordinate axes is

$$F_\gamma = c_\gamma \frac{q_{yz}^{(0)}}{V_0} \frac{1}{l_{\text{cube}}}, \quad (4)$$

where $q_{yz}^{(0)}$ is a component of the unit cell quadrupole moment, V_0 is the unit cell volume, whereas $c_x = c_y = -3.336$, while $c_z = 5.004$. Using this field and assuming an overall linear scaling of fields inside the cubic nanocrystal, one can qualitatively estimate the lineshape-size dependence. In general, the electric field associated contribution to the EFG is small, $g_{\alpha\beta,\gamma}F_\gamma \ll V_{\alpha\beta}^{(2)}$, so that the NQR frequency can be shown to be approximately linearly proportional to F_γ . Then, one can easily deduce also a linear relationship between the linewidth and the surface field. The proportionality of the later with $1/l_{\text{cube}}$ is thus reflected in the $\Delta\nu_{1/2} \propto 1/l$ dependence.

To check the influence of the used Sternheimer approximation on the lineshapes, we made two additional lineshape calculations for an $l = 100$ cube: one by increasing the series expansion with the $g_{\alpha\beta,\gamma\delta\epsilon}F_{\gamma\delta\epsilon}$ terms and thus improving the approximation, while the other by removing $g_{\alpha\beta,\gamma\delta}F_{\gamma\delta}$, and thus worsening the approximation. The improved approximation resulted in unnoticeable change of the lineshape. It thus appears that most of the changes are efficiently buried by the smoothing function. A shorter series expansion, on the other hand, produced an overall shift of the lineshape by 3.2 kHz, whereas the lineshape remained essentially unchanged. Based on these calculations, we also conclude that the electric fields through the shieldings $g_{\alpha\beta,\gamma}$ are the main agent of the NQR size-dependent lineshape broadening, whereas the contributions of other terms ($g_{\alpha\beta,\gamma\delta}$) are very small.

The assumption most seriously affecting our calculations is the use of a single charge distribution for all the urea molecules in the nanocrystal, apart for the embedded molecule of interest. As we have seen, for spheres, the electric fields are actually zero, so that the assumption seems quite justified. In cubes, however, the electric fields are inhomogeneous, and the urea dipole moment (quadrupole as well) will depend on the position of the molecule within the crystal. This variation significantly complicates calculations and its inclusion in calculations was out of the scope of this work. Nevertheless, we can simply estimate the size of the effect on the ν_+ frequency. Using Eq. (4), the unit cell quadrupole moment $|q^{(0)}| \approx 76$ and $V_0 = 1011.56$, both in atomic units, we can calculate the electric field on the cube's surface. For $l_{\text{cube}} = 100c$ we obtain $|E_{\text{cube}}| \approx 0.4 \cdot 10^{-3}$ atomic units. Then, using the calculated linear polarizability for urea²⁵ of $\bar{\alpha} = 35.61$ in atomic units gives a change of the dipole moment by $\epsilon = \bar{\alpha}E_{\text{cube}}/p_z \approx 0.5\%$ at the surface compared to the one in the center of the cube, where the electric field is zero. This number might not seem substantial at first, but a very rough estimate for the corresponding change of the NQR frequency is $\epsilon\nu_+ \approx 15$ kHz, which is much larger than the here found $\Delta\nu_{1/2} = 2.3$ kHz for an $l = 100$ cube. However, the problem is inherently nonlinear and $\epsilon\nu_+$ only suggests that this mechanism should be included in the calculations, especially for non-spherical geometries.

Inevitably the lineshape of a real sample will be broadened also by some other mechanisms, which we have not taken into account in this study. For example, the nanocrystals might include lattice imperfections, strains, impurities. . . all well known broadening mechanisms. In addition, the here used approximation completely neglects all molecular motions and lattice vibrations, which can also induce broadening/narrowing. And finally, our model of isolated nanocrystals is certainly very difficult to experimentally realise, meaning that neighboring nanocrystals will mutually influence each other, most likely by introducing additional broadening. Some of these mechanisms can be rather easily removed experimentally, e.g., by meticulous sample preparation or by cooling the samples, whereas others, like nanocrystal-nanocrystal interaction, might be more difficult to remove. Nevertheless, the here calculated linewidth is at the core of the size-induced broadening and should serve as a reference for other mechanisms.

IV. CONCLUSIONS

We have used *ab initio* techniques to find the electric field gradient (EFG) tensor for each nitrogen site in the urea nanocrystals of two geometries, spheres and cubes, of various sizes, where we used the embedded molecule approach to include the crystal fields. The influence of distant molecules was found using a Sternheimer series expansion, whose coefficients were calculated within this study with the *ab initio* finite field method. The found EFG tensors were used to form the ^{14}N ν_+ lineshape of the NQR spectrum.

We find that the ν_+ lineshape mean frequency is practically independent of the nanocrystal size and geometry, and corresponds to the frequency in bulk. The ν_+ linewidth, on the other hand, is size dependent: for both geometries, it decreases as the nanocrystal size is increased, as expected. However, there is a striking difference between the linewidths of the two geometries. For cubes, we find a smooth $1/\text{size}$ dependence; for sizes <10 nm the lineshape is probably too broad to be observed with pure NQR techniques, for a size ~ 10 nm, it is ~ 12 kHz, but even for the size ~ 100 nm, the lineshape is still considered broad by the ^{14}N NQR standards, as it is ~ 2 kHz wide. The lineshape for spheres is narrow and is within the ^{14}N NQR observation window already for the smallest nanocrystals studied here, ~ 5 nm, where it is ~ 12 kHz. For a larger nanocrystal, the linewidth quickly drops to a negligible value, determined here by the used broadening function (22 Hz). Thus, spherical nanocrystals should almost always yield very sharp ^{14}N NQR resonances. We thus foresee that ^{14}N NQR spectroscopy is a viable technique to study nanocrystals; however, its applicability is expected to be variable, depending on the nanocrystals size and geometry.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for point multipole expansion of the urea molecule in bulk calculated with the embedded molecule approach at the MP2 level for basis sets aug-cc-pVDZ and aug-cc-pVTZ.

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